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Spectrographic Analysis of Trace Elements In Aluminum Oxide Matrices

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ELECTRONIC MATERIAL SCIENCES LABORATORY PROJECT 5620

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Abstract

Twenty-five trace elements in aluminum oxide matrices are determined by a spectrographic method. The oxide samples buffered with graphite are arced at high amperage and the spectral intensities measured by an external standard, pure aluminum oxide, excited similarly. The method is convenient, sensitive, precise, and more suited than chemical analysis, which would require an extended, difficult, and complex analytical scheme. It has been used routinely for the analysis of lasers and related materials. The concentration ranges covered for the impurities vary from 0.0001 and 0.0025 up to 0.010.

Acknowledgment

The author is indebted to Mr. B. Spada for the fabrication of the Stallwood Jet used under this method.

Contents

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1. INTRODUCTION

Nowhere is the effect of trace impurities more dramatically demonstrated than in the solid state. The concentration and control of impurities are essential to semiconductor technology. More recent developments in the field of ultrapure materials are again emphasizing the role that trace impurities play in determining physical characteristics.[1] This is particularly true in the case of synthetic rubies used for lasers, where a real need exists for a rapid and comprehensive chemical analysis.

The samples discussed in this paper include the rubies and the calcined aluminum salts used in their preparation. A preliminary examination of these compounds by spectrographic means indicated that the vast majority of the impurities present were below 100 ppm. Notable exceptions to this were the elements chromium, magnesium, and silicon. A total of 25 elements was observed in various samples; however, the average number per sample was 10.

The refractory nature of aluminum oxide and the skill, time, and manpower required by a laboratory to analyze this material precluded its solution by classical methods. An especially objectionable feature of a "wet chemical" attack of this problem is the high flux ratio required for the chemical dissolution of aluminum oxide with the resultant large reagent blanks. Because of these factors, the chemical approach was eliminated from consideration

The best solution appeared to be the emission spectrograph, an analytical tool

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ideally suited for this scope and concentration range (1 and 100 ppm) of the desired impurity elements.

2. PROCEDURE

The accepted method for making accurate quantitative determinations by spectrochemical means is the use of an internal standard. Inherent with internal standardization is consideration of all the factors[2] governing proper choice. The large number of impurity elements sought in these samples eliminated the use of internal standardization. Therefore the "external standard" approach to the problem along the lines of Hampton[3] and Slavin[4] was employed. These investigators used cobalt oxide and a constant intensity iron arc, respectively, as external standards to measure spectral intensities. The "external standard" method requires a reproducible unit of intensity. The sectored source is recorded on each plate for the purposes of calibration, since the intensities are compared for various plates rather than by relative intensities used in the "internal standard" method. Here aluminum oxide was chosen for the external standard, since weighed portions of the pure aluminum oxide and samples yielded similar exposure times for identical excitation conditions (Table 2). The paucity of aluminum lines for calibration purposes over the wavelength under study dictated the use of an emulsion with a relatively constant gamma for this particular region.

Three dozen Eastman SA-2 plates from the same emulsion batch were set aside for this work. An experimental examination of the gamma by conventional calibration techniques at 50 Å increments showed it to be almost constant from 2400 to 4500 Å. Thus only one calibration curve was required for the entire wavelength range.

In addition to being refractory, aluminum oxide displays the objectionable feature of beading when burned in the d-c arc, further increasing exposure times. Beading may be overcome by the addition of a buffer such as graphite; and, if the initial sample size is kept small, reasonable exposure periods are achieved. The oxide (5.0 mg) mixed with an equal amount of graphite and arced at 16 amperes in a Stallwood Jet[5] produced optimum results. A test on a dozen samples using these conditions yielded exposure periods of 30 ± 2 seconds.

The weighed external standard (5.0 mg Al_2O_3 + 5.0 mg graphite) was arced for 35 seconds (completion) with a 7-stepped sector (step ratio 1:2) placed at the stigmatic position of the spectrograph. Sectored steps of the Al 3059.933 Å line were read on the densitometer and plotted using log-log coordinates versus equivalent mg Al_2O_3. Although the reproducibility of this graph proved to be excellent, it was recorded on each plate used in this work.

With this calibration curve, the analytical working curves in Figures 1, 2, and

3 were constructed. Both standards and samples were weighed (5.00 mg) on a semi-micro balance to within ± 0.01 mg, the spectral intensity measurements adjusted for background and sample weight, and the points on the working curves determined from an average based on four exposures for each concentration. A variable aperture rotating sector was used for recording spectrograms at 100% and 50% transmittance, thereby extending the useful range of analysis lines.

3. PREPARATION OF STANDARDS

Since no aluminum oxide standards existed in this concentration range, a series of synthetic ones were prepared. Johnson and Mathey Company "Specpure" aluminum oxide was used as the base material. The impurity elements in the form of oxides were blended into the base material by grinding in a boron carbide mortar. Additional mixing was accomplished by tumbling for 24 hours.

Previous to grinding, only magnesium and silicon were observed in the base material. After grinding, boron also appeared. Blank values estimated according to the method of Oertel[5] are indicated in Table 1.

By successive dilution with pure Al_2O_3, 8 standards were made to cover the concentration range between 0.0001 and 0.01.

4. PRECISION AND ACCURACY

There were no aluminum oxide standards available at this concentration range for precision and accuracy measurements.

Therefore a synthetic sample containing 25 impurities was made for this purpose. The precision data in Table 3 are based on 8 arcings of this sample. At this time, there is no measure of the accuracy available, for the reasons previously stated.

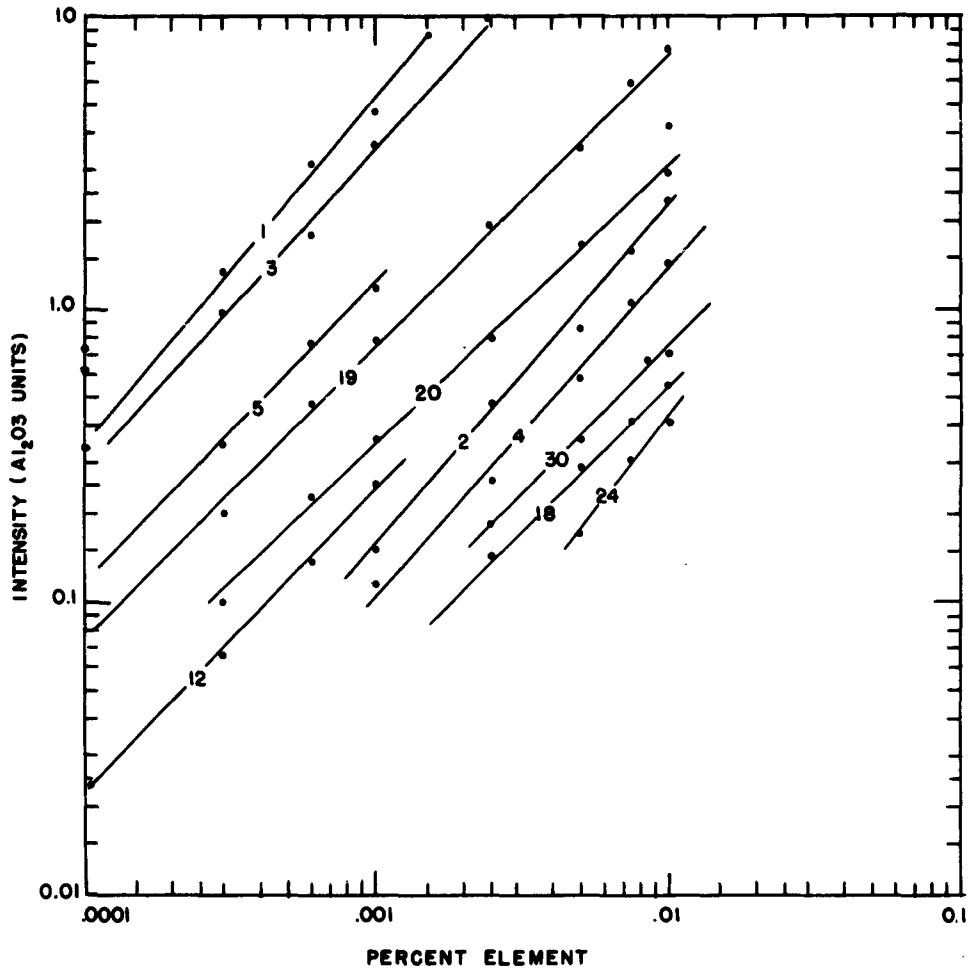

Figure 1. Analytical Working Curves

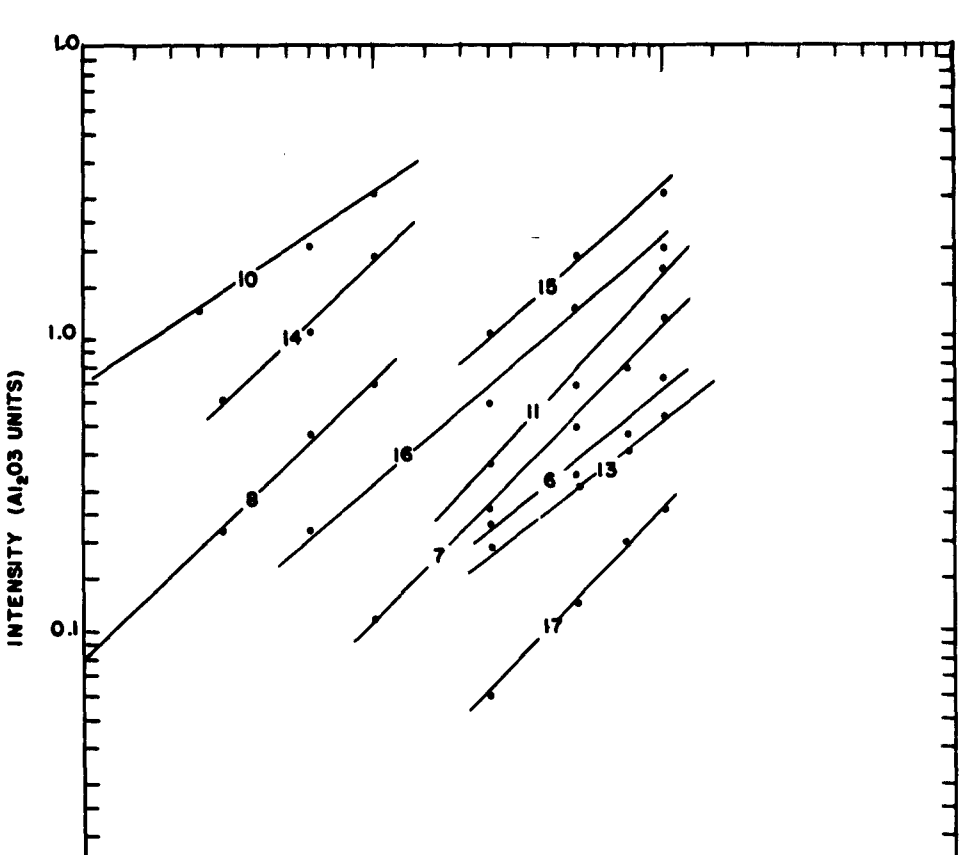

Figure 2. Analytical Working Curves

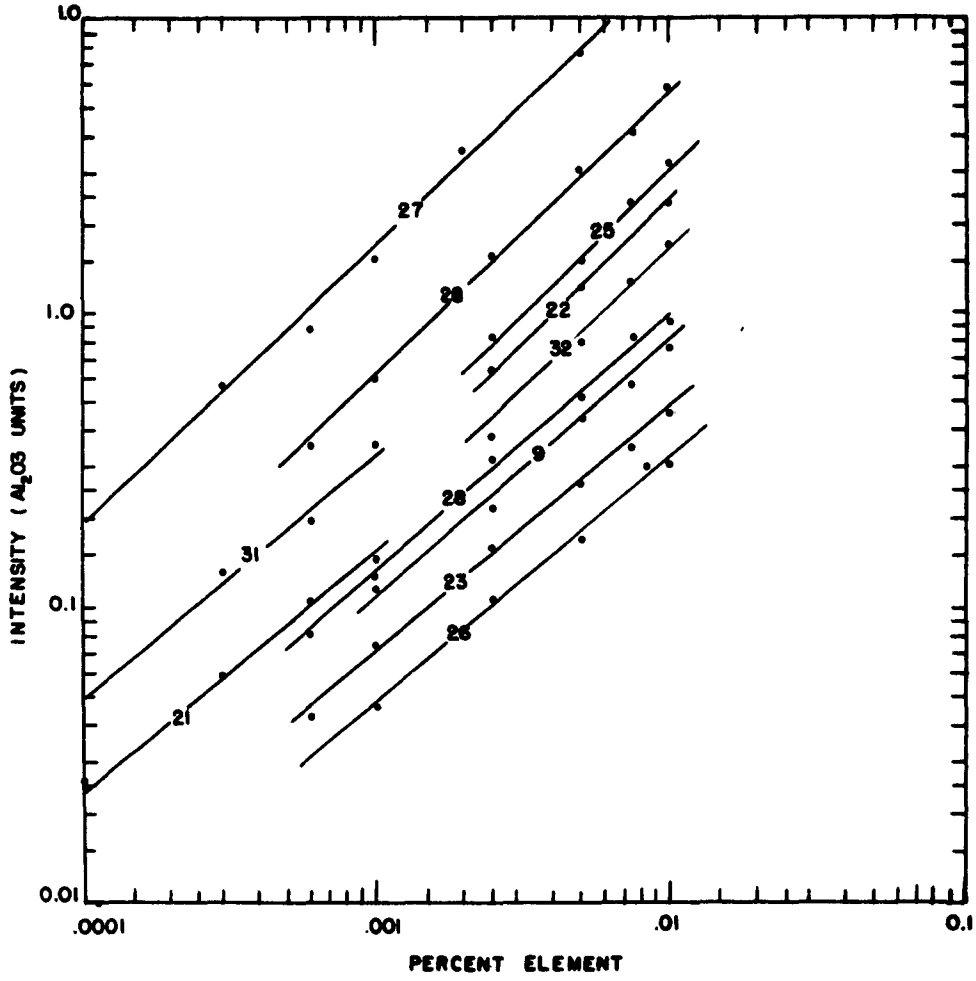

Figure 3. Analytical Working Curves

TABLE 1. Equipment

Spectrograph	Baird-Atomic Three Meter Eagle Mount with quart spherical condensing lens.
Source	Baird-Atomic Multi-Source providing 1-30 amperes d-c with an open circuit voltage of 300 volts.
Plates	Eastman Kodak type SA-2.
Densitometer	Jarrel Ash Co. Comparator - microphotometer.
Electrodes	Anode C-400, Cathode 1992 manufactured by United Carbon Products Co.
Photographic	Jarrell Ash Co. Constant Temperature Processing Unit.

TABLE 2. Spectroscopic conditions

Amperage	16
Analytical Gap, mm	6
Stallwood Jet	Ar/O_2 (70 /30)
Gas Flow Rate, 1/min	5
Slit width, μ	25
Slit height, mm	1.5
Preburn, sec	None
Exposure, sec	35
Spectral Range, Å	2400 -4400
Rotating sector, %T	50, 100
Photographic Processing	(1) 5 min at 20°C in D-19 (2) 30 sec in SB-5 stop bath (3) 5 min in Kodafix (4) Washed in water for 20 min

TABLE 3. Spectral lines, range and precision

Element[c]	Wavelength A (4)	Range	Precision[a]
Ag (1)	3280.683	0.0001 - 0.01	20
B[b] (2)	2496.778	0.0025 - 0.01	8.6.
Be (3)	2348.610	0.0001 - 0.01	27
Bi (4)	3067.716	0.001 - 0.01	12
Ca (5)	4226.728	0.0001 - 0.001	15
Ca (6)	3179.332	0.0025 - 0.01	25
Cd (7)	3261.057	0.001 - 0.01	7.8
Co (8)	3453.505	0.0001 - 0.001	16
Co (9)	2411.622	0.0025 - 0.01	21
Cr (10)	4254.346	0.0001 - 0.001	9.8
Cr (11)	2835.633	0.0025 - 0.01	12
Cu (12)	3247.540	0.0001 - 0.001	10
Cu (13)	2592.627	0.0025 - 0.01	19
Fe (14)	3020.640	0.0001 - 0.001	11
Fe (15)	2483.270	0.0025 - 0.01	22
Ge (16)	2651.575	0.0006 - 0.01	19
Hg (17)	2536.519	0.0025 - 0.01	30
Mg[b] (18)	2779.834	0.0025 - 0.01	19
Mn (19)	2593.729	0.0001 - 0.01	11
Mo (20)	3193.973	0.0003 - 0.01	20
Ni (21)	3414.765	0.0001 - 0.001	8.6
Ni (22)	3002.491	0.0025 - 0.01	14
Pb (23)	2833.069	0.0006 - 0.01	17
Sb (24)	2598.062	0.0050 - 0.010	18
Si[b] (25)	2506.899	0.001 - 0.01	32
Sn (26)	3262.328	0.001 - 0.01	18
Ti (27)	3234.516	0.0001 - 0.01	9.5
V (28)	3102.299	0.0006 - 0.01	26
W (29)	3215.560	0.001 - 0.01	17
Zn (30)	3282.333	0.0025 - 0.01	14
Zr (31)	3391.975	0.0001 - 0.001	8.4
Zr (32)	2571.39	0.0025 - 0.01	14

[a]Precision expressed as the coefficient of variation, v, is determined as follows:

$$V = \frac{100}{C}\sqrt{\frac{d^2}{n-1}}$$

where

C = average concentration, in percent

d = difference of the determination from the mean, and

n = number of determinations

[b]Lower concentration blank value

[c]Element numbers identify individual working curves in Figures 1, 2 and 3.

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